

# Detection of nanocracks on double fluoride rare earth crystal surface

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## Abstract

Predicted earlier, microcracks on the crystal surface of both finely dispersed  $LiYF_4$  powders and single crystals of the Van Vleck paramagnet  $LiTmF_4$  were detected by using the NMR Cryoporometry and Atomic-Force Microscopy technique.

In paper [1], in order to explain the specific features of the liquid  $^3He$  magnetic relaxation in its contact with single crystals of the dielectric Van Vleck paramagnet  $LiTmF_4$  and its diamagnetic analog -  $LiYF_4$ , we suggested the following hypothesis: On the surface of these crystals, microcracks exist with an average size near 10 nm. In these microcracks the character of diffusion motion of  $^3He$  atoms was supposed to change drastically. In such a bounded geometry, the atoms of  $^3He$  determine, in fact, the kinetics of magnetic relaxation of the liquid  $^3He$  which is in contact with a solid body substrate. In this work we present our results on the detection of the microcracks, their size being near 30nm (called "nanocracks"). This was obtained as the result of the two independent methods - the NMR Cryoporometry and the Atomic-Force Microscopy (AFM).

For investigation by means of the NMR Cryoporometry, the three finely dispersed LiYF<sub>4</sub> samples with typical sizes: 700 nm (sample-I), 900 nm (sample-II), and 4000 nm (sample-III) were prepared. The technique of powder preparation can be found in [2]. All samples were immersed in their own containers, the packing factor being about 0.5. The prepared samples can be considered as a porous body containing a three-dimensional net of channels of various dimensions and forms, i.e., in fact, it can be considered as a single pore with a very complicated geometry. For analysis purposes such a space is usually partitioned into a set of pores of various sizes, the pores being assumed to be connect to each other. In this situation, by the term "pore size" the least distance between opposite walls of a pore is understood. The distribution of the pores with respect to their sizes is usually determined by means of the gas absorption and mercury porometry methods. However, both the methods require long time measurements, rather complicated procedures, and precise experimental equipment. On the other hand, it is well known that the physical properties of a liquid bounded by microscopic pores strongly differ from those of a bulk liquid (see, for example, [3],[4]). In part, the melting temperature can lower due to increasing contribution from the relative part of the surface free energy ( for example, the melting temperature of  $H_2O$  may occur 60 K lower in a media with average pores about 2 nm, see [5]). This phenomena lies in the base of pores distribution measuring by means of the NMR of water protons. The part of the liquid phase and the corresponding size of pores are determined by the intensity of the pulse-NMR of protons with relatively greater spin-spin relaxation time  $T_2$ . Obtained in this manner, the dependence of the intensity of the NMR line on the temperature then can be transformed into a curve of pores distribution with respect to their size with help of the probe curve "change of melting temperature- pore size" (see [6]).

If we start with the assumption that powder particles are solid spheres with diameter 1000 nm, then, for a hexagonal dense packing, our estimates show that the pores whose size is less than 10 nm constitute a part which is less than 1% of the whole quantity. Therefore, we can assert *a priori* that greater values of the specific weight will demonstrate the presence of developed microrelief on the surface of crystal particles.

The curves of the pore size distribution were obtained by using the data of the impulse NMR of the distilled water protons on the frequencies 20 MHz (a home-made spectrometer) and 80 MHz (Bruker NMR spectrometer W80) for all three samples. This data is shown on the Fig. 1a. Obviously, if the nanocracks have no place, the graph distribution has to have a functional dependence of the type  $D^\alpha$ , where  $D$  stands for the characteristic size of pores, and the exponent  $\alpha$  exceeds 1. Our experimental data show that the nanocracks are evidently present on the surface of particles. As one can see on Fig 1b, the distribution has two maximums which correspond to the specific porous sizes of 3-5nm

and 15-20nm, their part occupying near 20% of the whole hollow volume of the sample.

To visualize the microrelief of a particle surface, we carried out investigations of the particles of the sample-III by means of the Atomic-Force Microscope P4-SPM-MDT (produced by NT-MDT, Zelenograd, RF). The construction of the microscope allows to assert the presence of the nanocracks with a size greater than 30 nm. The AFM-images of various magnifications of a particle surface can be seen on Fig. 2. It is evidently seen that the surface possesses sufficiently developed microrelief.

One may suppose that the nanocracks appear due to the technique of powder preparation, namely, in view of the mechanical grinding. In this connection the investigation of the surface of a single crystal sample seems to be of interest. In view of our further investigations of the magnetic coupling between the liquid  $^3\text{He}$  and a solid-state substrate, we applied the AFM-investigation to a single crystal of  $\text{LiTmF}_4$ . The surfaces (100), (110), and (001) of the single crystal were mechanically polished in a certain direction with respect to crystallographic axes (the abrasive for coarse polishing had a grain 1030, while the finishing was made with the GOI-paste with particles smaller than 0.5). One of the AFM-pictures of the single crystal surface is shown on the Fig 3. Our experimental results do not show a correlation between the nanocracks' character and crystallographic planes. Obviously, the obtained surface microrelief cannot be conditioned as the only result of a mechanical polishing in a certain direction. Thus, investigations detect the presence of the nanocracks on the surface of both particles and single crystals. The most probable reason for the nanocracks' appearance is formation of local mechanical stresses in a sample sawing by a diamond-charged saw, which then are discharged due to surface reforming.

We should note that the crystal structure of double fluorides of rare earth has no cleavage planes. The AFM experiments carried out with single crystal  $\text{LiF}$  and  $\text{CaF}_2$  samples which have evident cleavage planes (100) and (111), respectively, showed the absence of nanocracks on the surfaces of a "fresh" cleavage.

The investigations carried out result in the established presence of nanocracks, predicted earlier by the authors (see [1]), and their distribution by size on  $\text{LiYF}_4$  and  $\text{LiTmF}_4$  crystal surface. This seems to be of importance for both the detailed investigation of the nature of magnetic coupling between liquid  $^3\text{He}$  and a solid-state substrate, on one hand, and the practical realization of a method of dynamic nuclei polarization of liquid  $^3\text{He}$  with the use of the dielectric Van Vleck paramagnets. This technique was suggested by the authors in [7]. From our results it follows that the surface of particles of finely dispersed powders is deformed in a high degree. The latter is in good correspondence with our estimates of the deformed layer part in systems of this kind (see [8]).

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## References

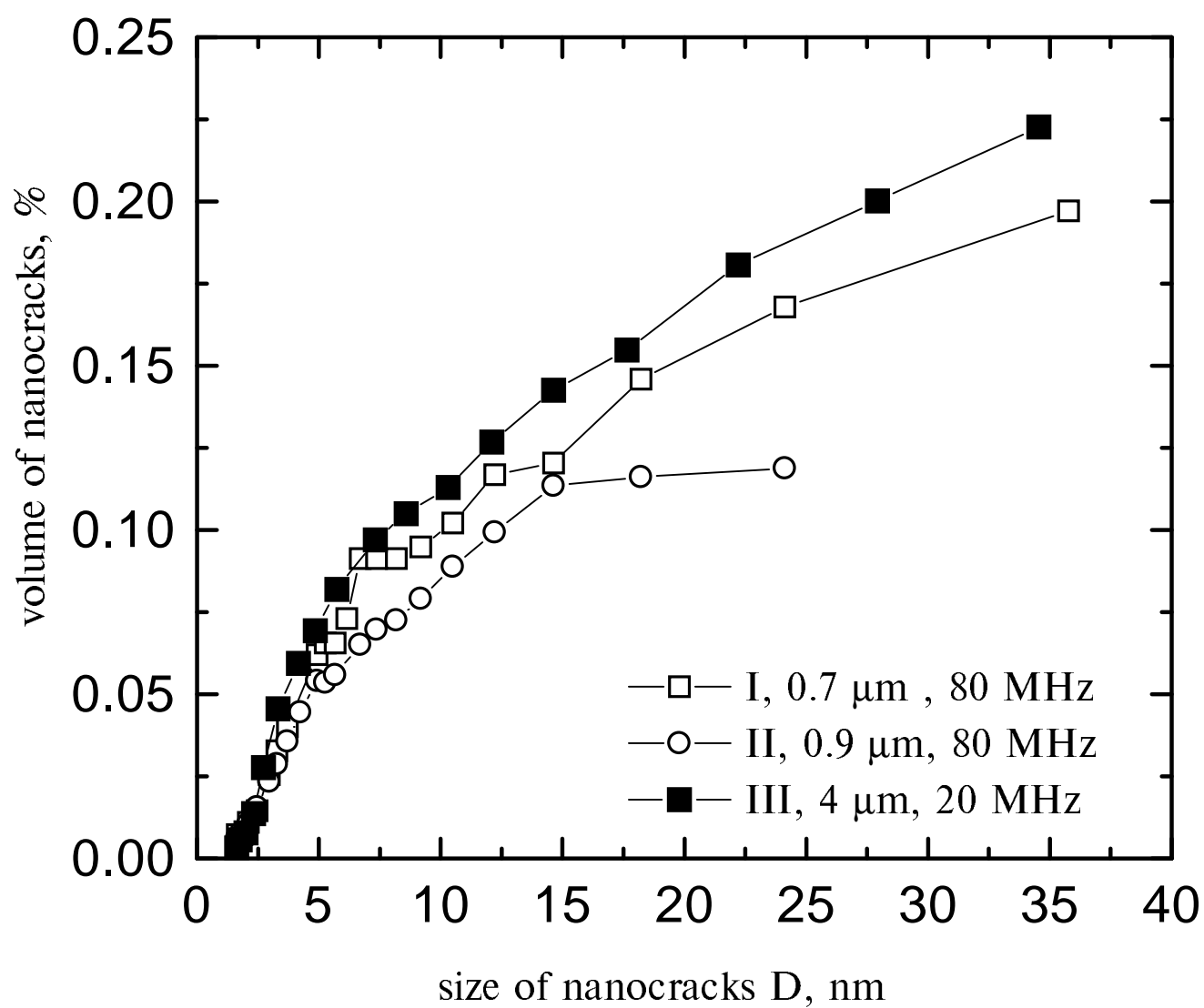
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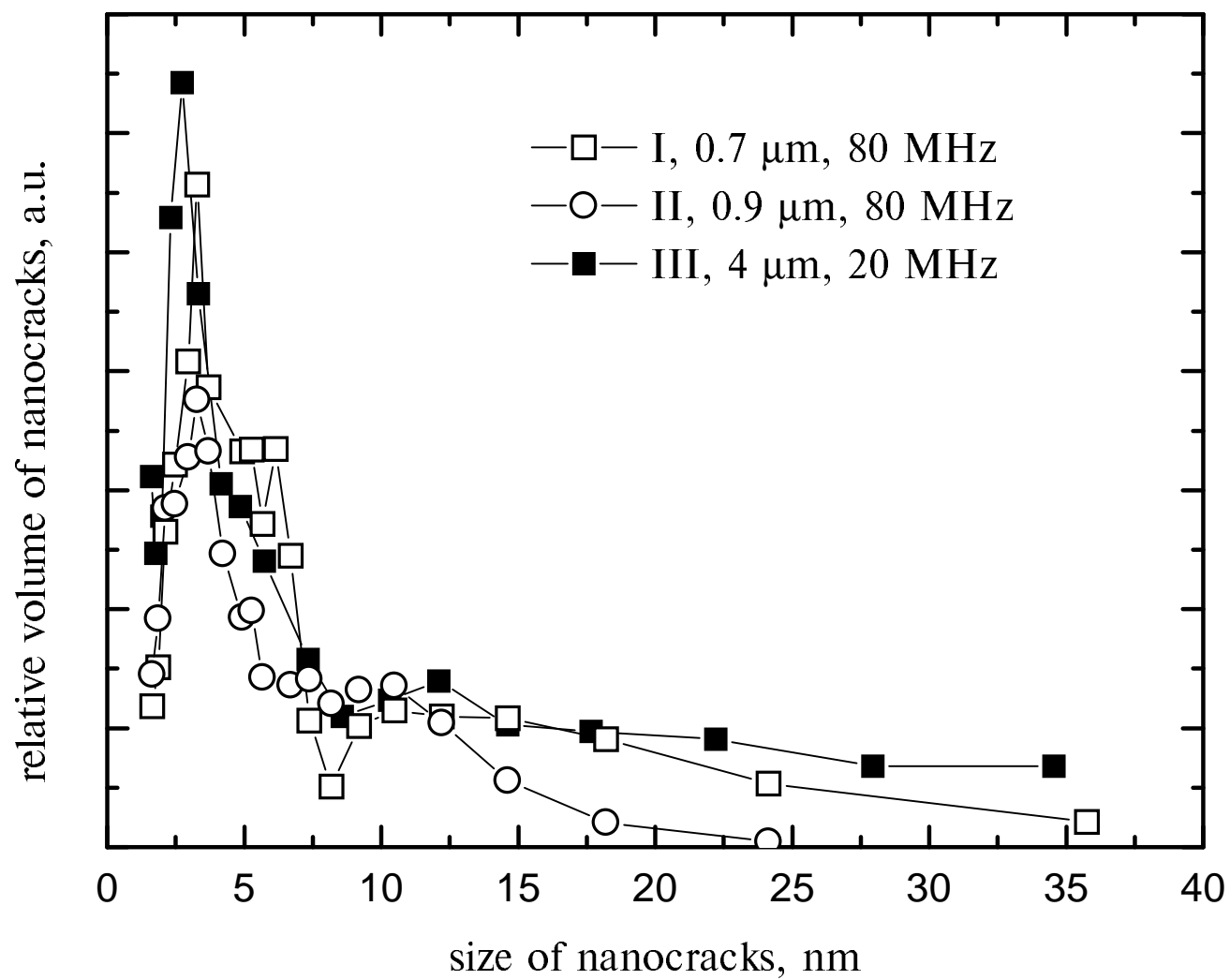
**Figure capture**

Fig.1. a) The relative volume of nanocracks in dependence on their size for three samples, obtained by NMR Cryoporometry. b) The distribution of nanocracks with respect to their size.

Fig.2. a), b) The picture of the surface of a particle of sample III, obtained by AFM; one division of the graduation scale is 100 *nm*.

Fig.3. The picture of the surface (110) of a single crystal  $LiTmF_4$ , obtained by AFM. Polishing was done along the *X*- axis, scanned along the *X*-axis. The graduation on both the axes *X* and *Y* is 1000 *nm*, on the axis *Z* -100 *nm*.







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